# Resist-outgas testing and EUV optics contamination at NIST

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# Outline

- Status and progress of resist testing at NIST
- Summary of previous contamination studies at NIST
- Atomic-H cleaning of carbon and non-C residuals
- Future directions

# Update on resist-outgas testing at NIST

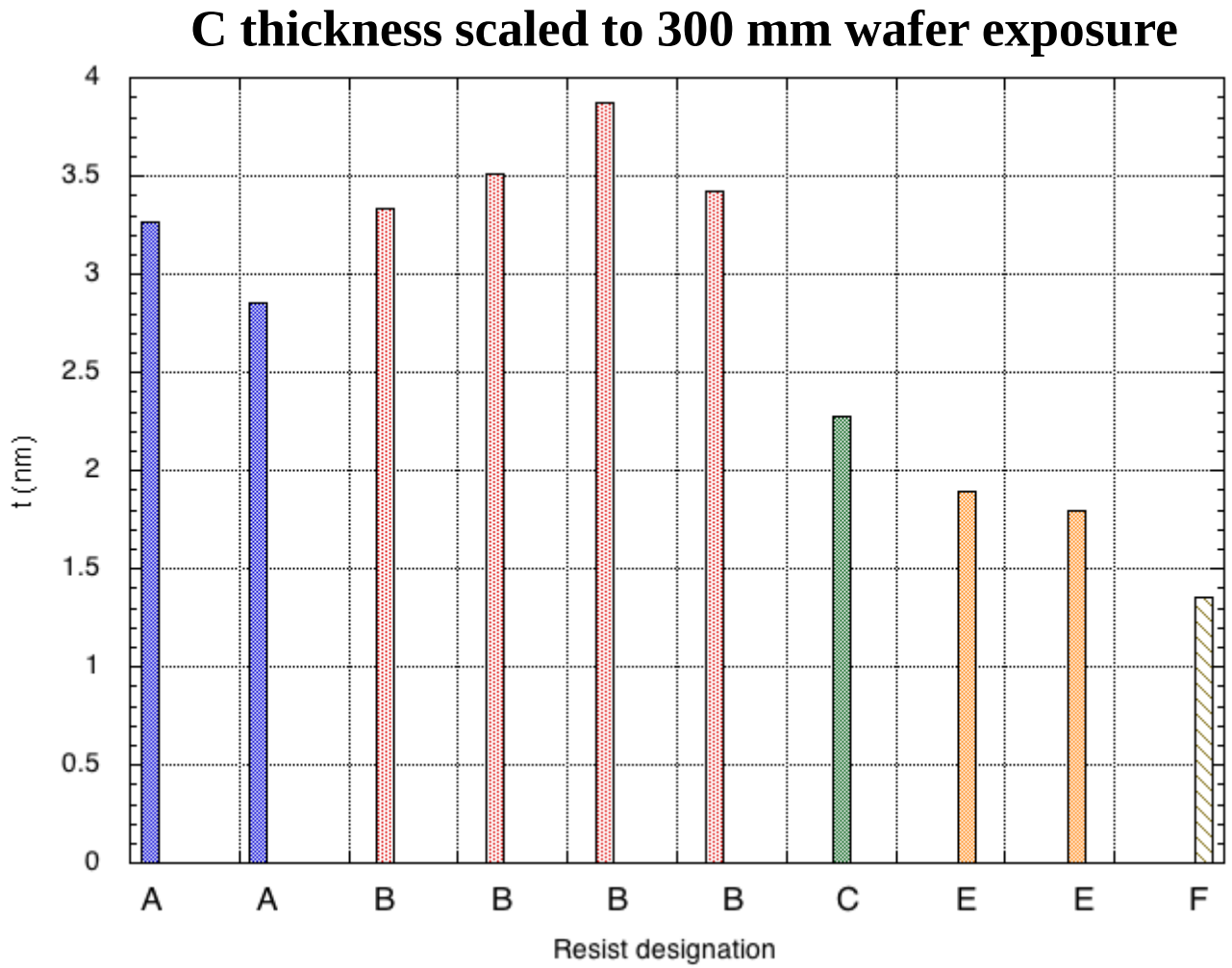
- Agreements to perform testing with four resist manufacturers

- NIST witness sample (WS) resist-outgas test
  - E0 measurement
  - Includes 2 separate WS exposures to verify reproducibility
  - Cost  $9,363 per resist
  - Current throughput ≈ 1.5 resists per week

- Once reproducibility is sufficiently established over several resist families, cost will be lowered & throughput increased by performing only one WS exposure per resist.

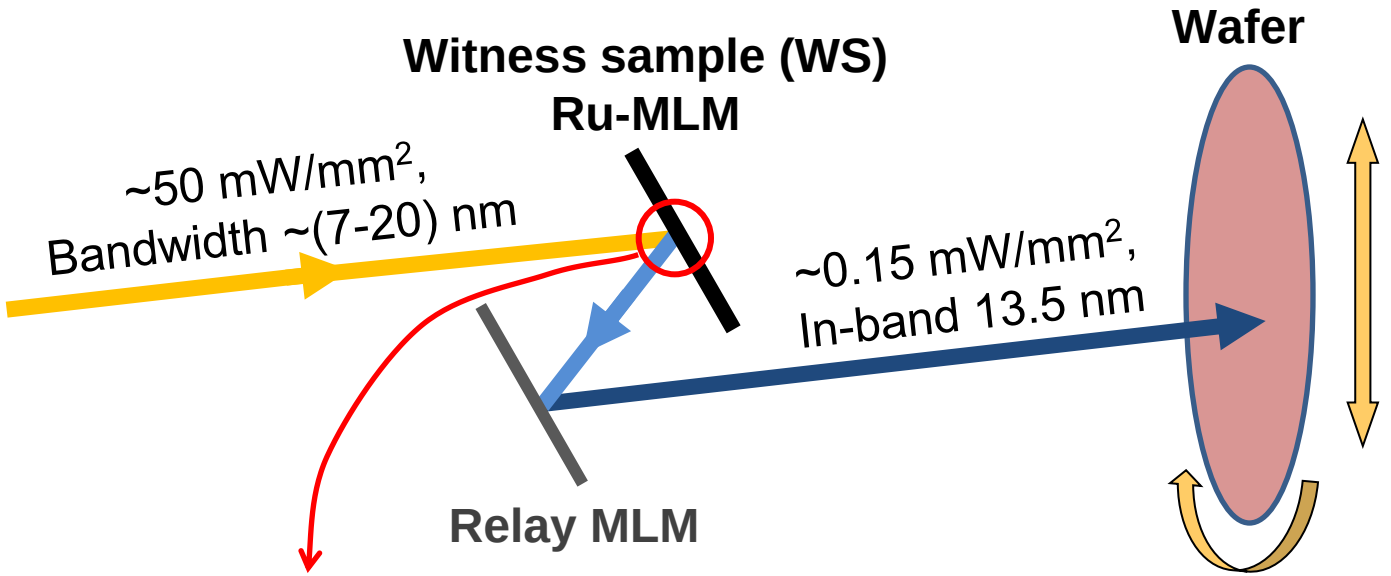
- Limited data base of 10 different resists tested to date
  - Only one failed NXE-3300 C thickness spec
  - 5 tests of commercial resists (all passed)

# 5 resists tested during qualification of NIST facility

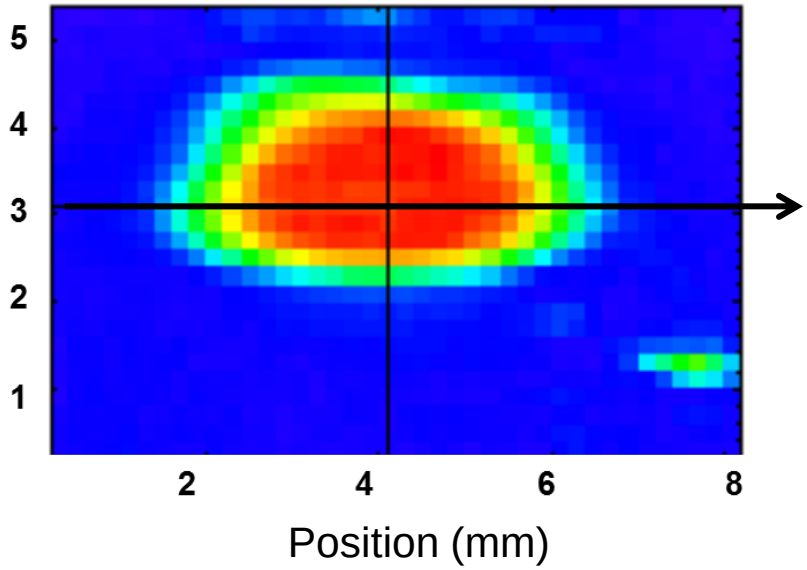



- 200 mm wafer exposed in 1 hr
- C thickness scaled by 9/4 to get 300 mm wafer exposure equivalent
- Reproducibility within ±10%

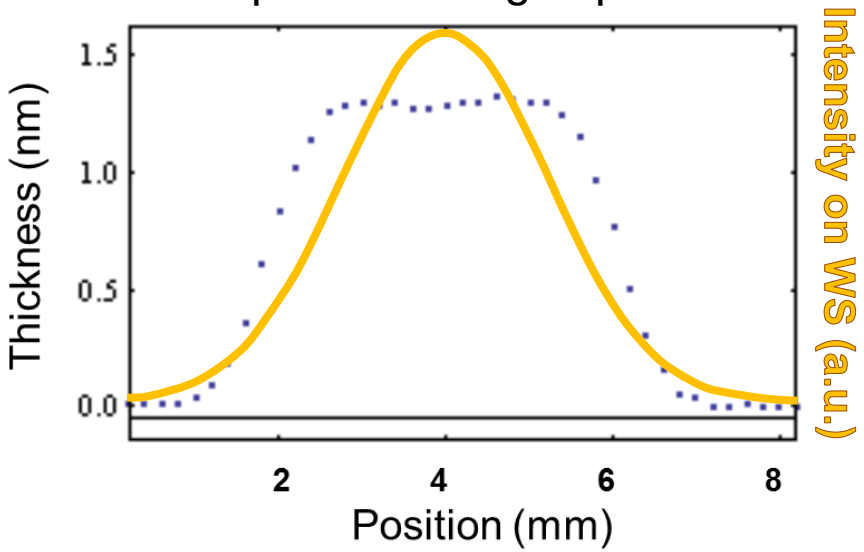
# Outgas testing requires intensity saturation on WS



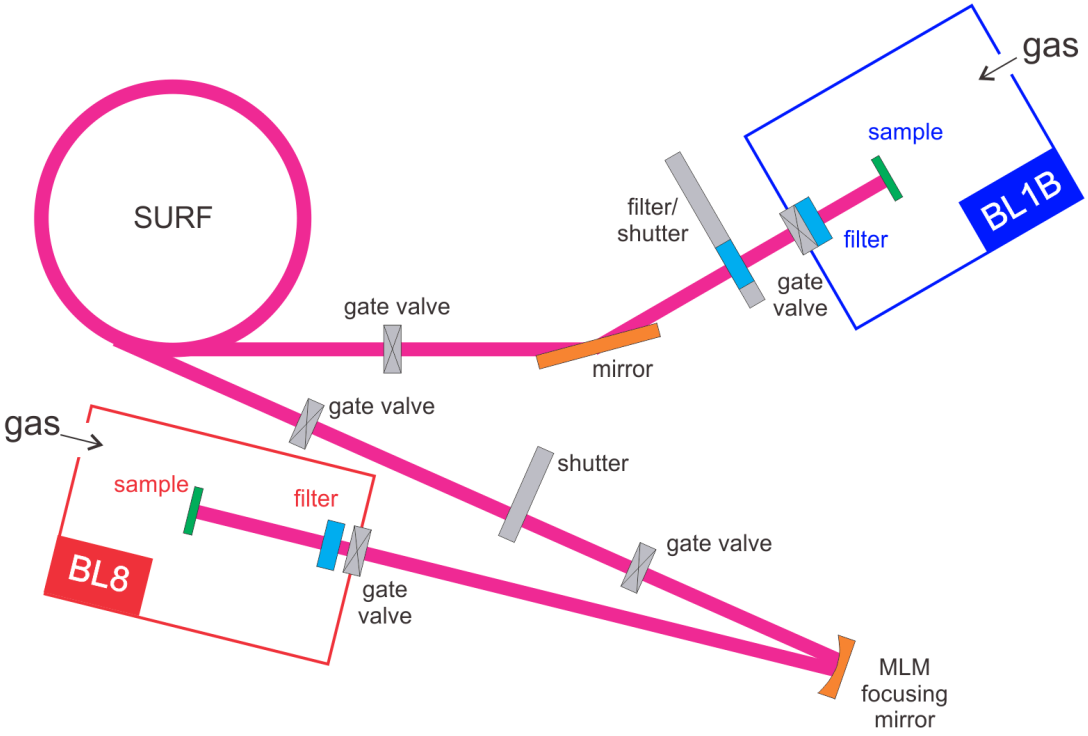

Spectroscopic ellipsometry map

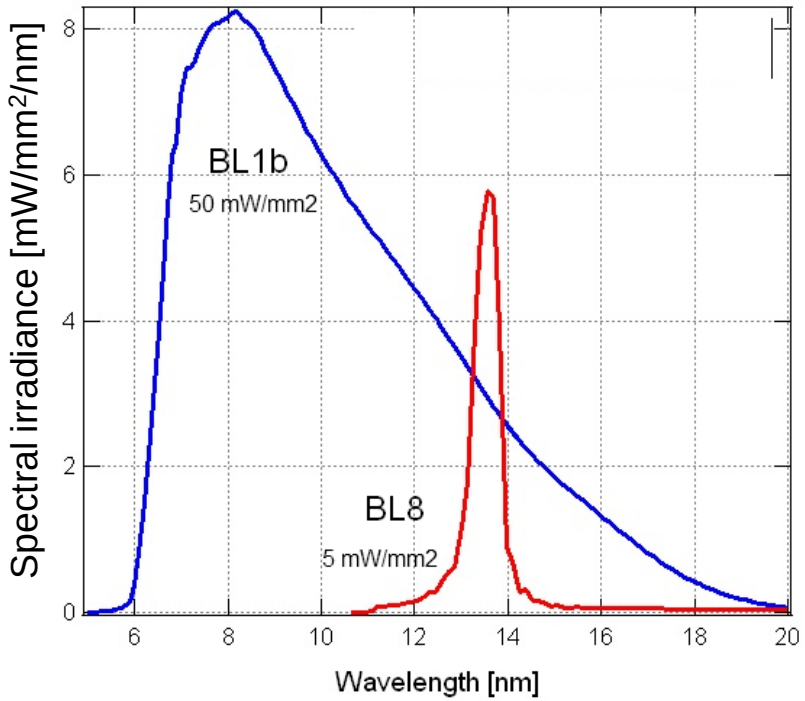



Line profile through spot center



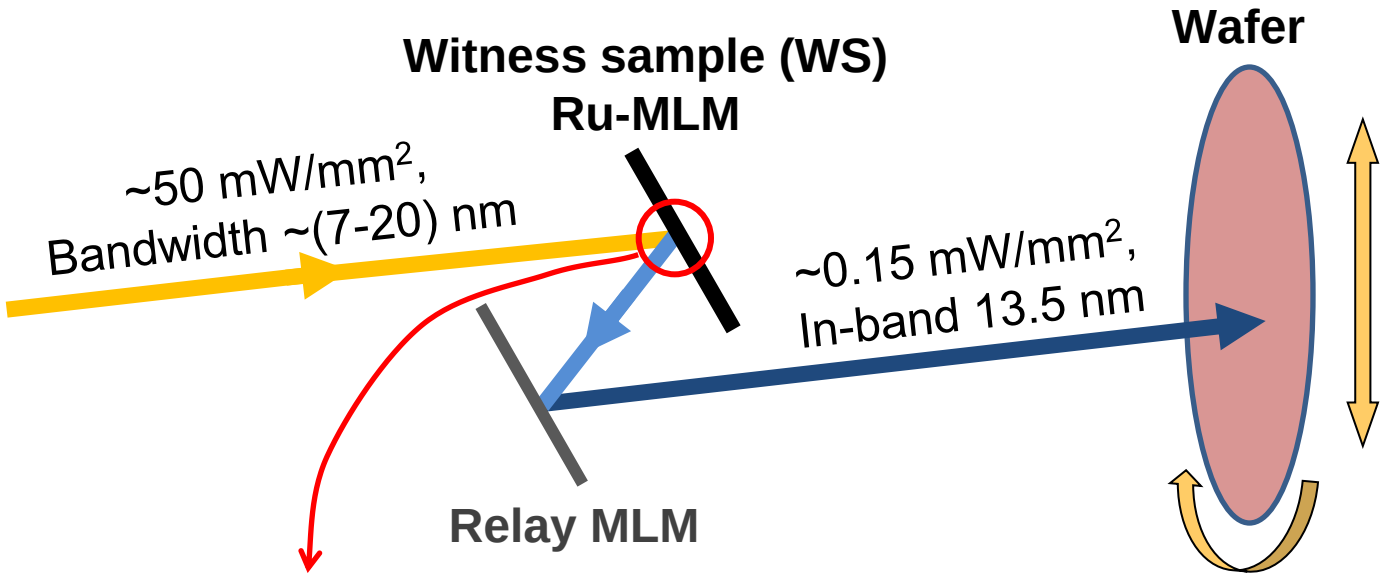
# Admitted-gas studies at NIST



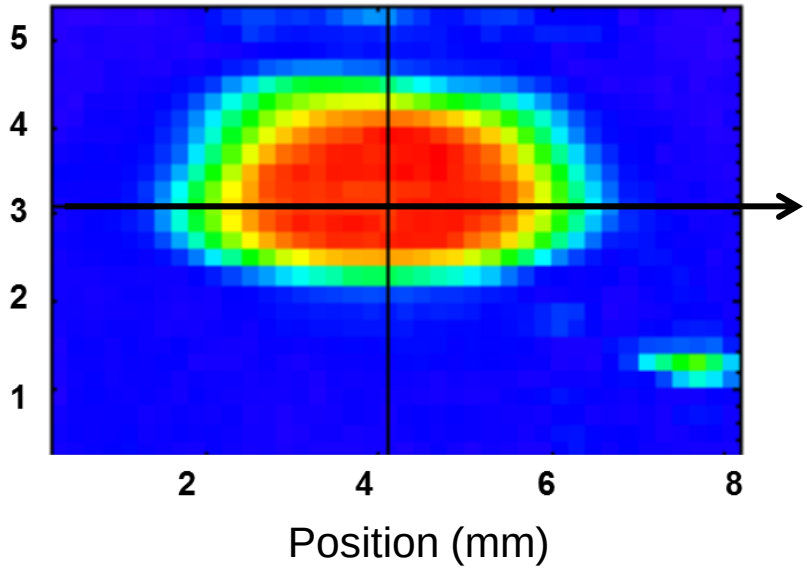




- Two optics-contamination beamlines at NIST synchrotron
  - BL1B: high intensity (50 mW/mm$^2$), broadband with median wavelength 10 nm
  - BL8: moderate intensity (5 mW/mm$^2$), in-band at 13.5 nm
- Established basic scaling laws for EUV-induced contamination rates
  - Intensity
  - Pressure
  - Species
  - Wavelength

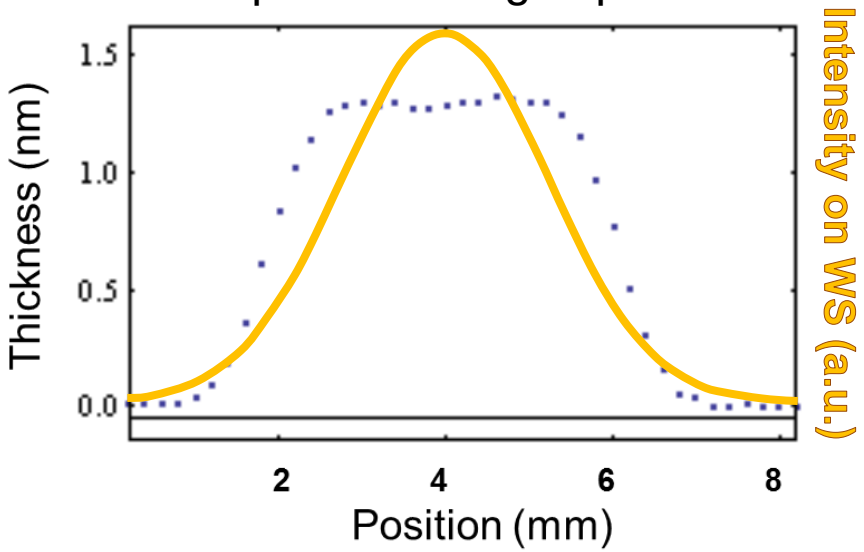
# Studies of intensity dependence of contamination rates



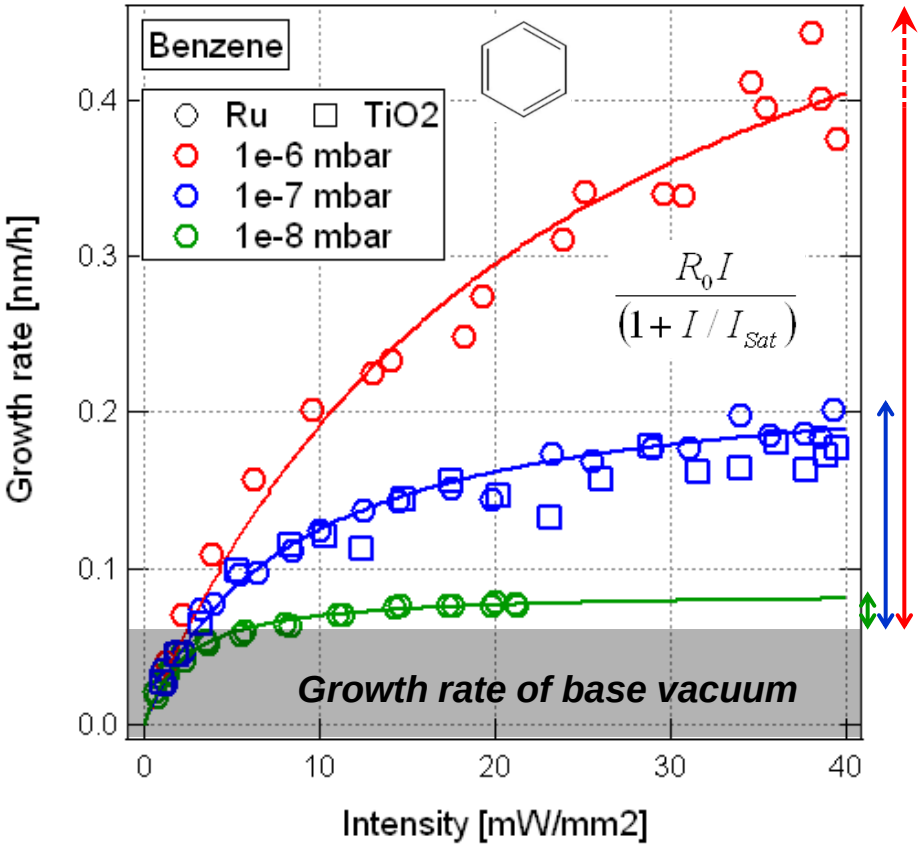

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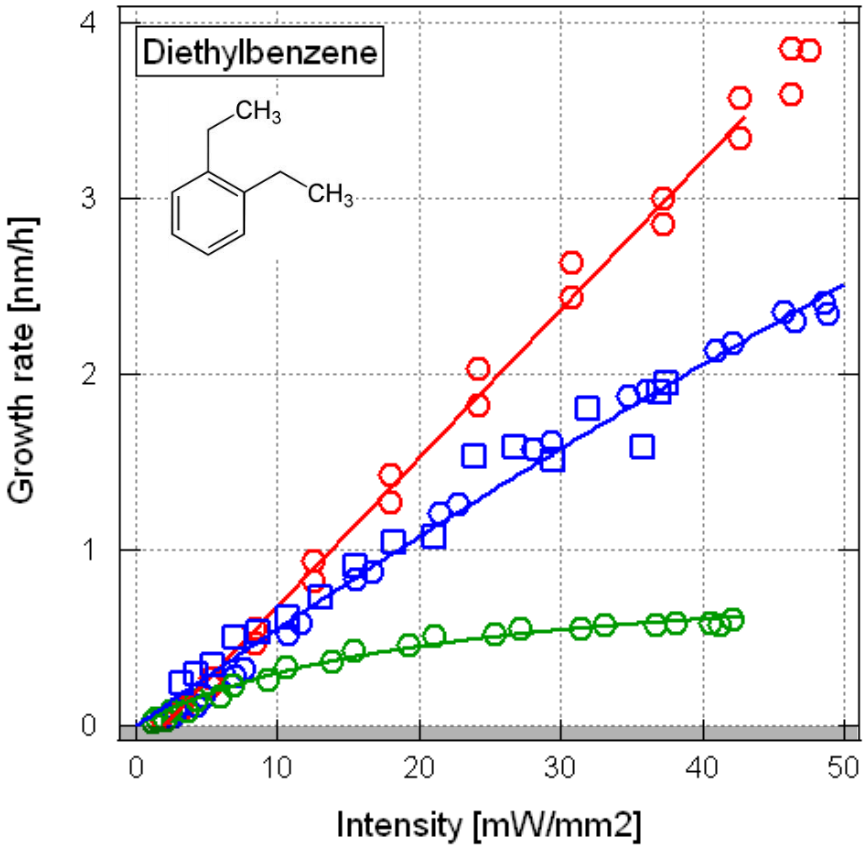



Line profile through spot center



# Intensity scaling: saturation & mass-limited growth

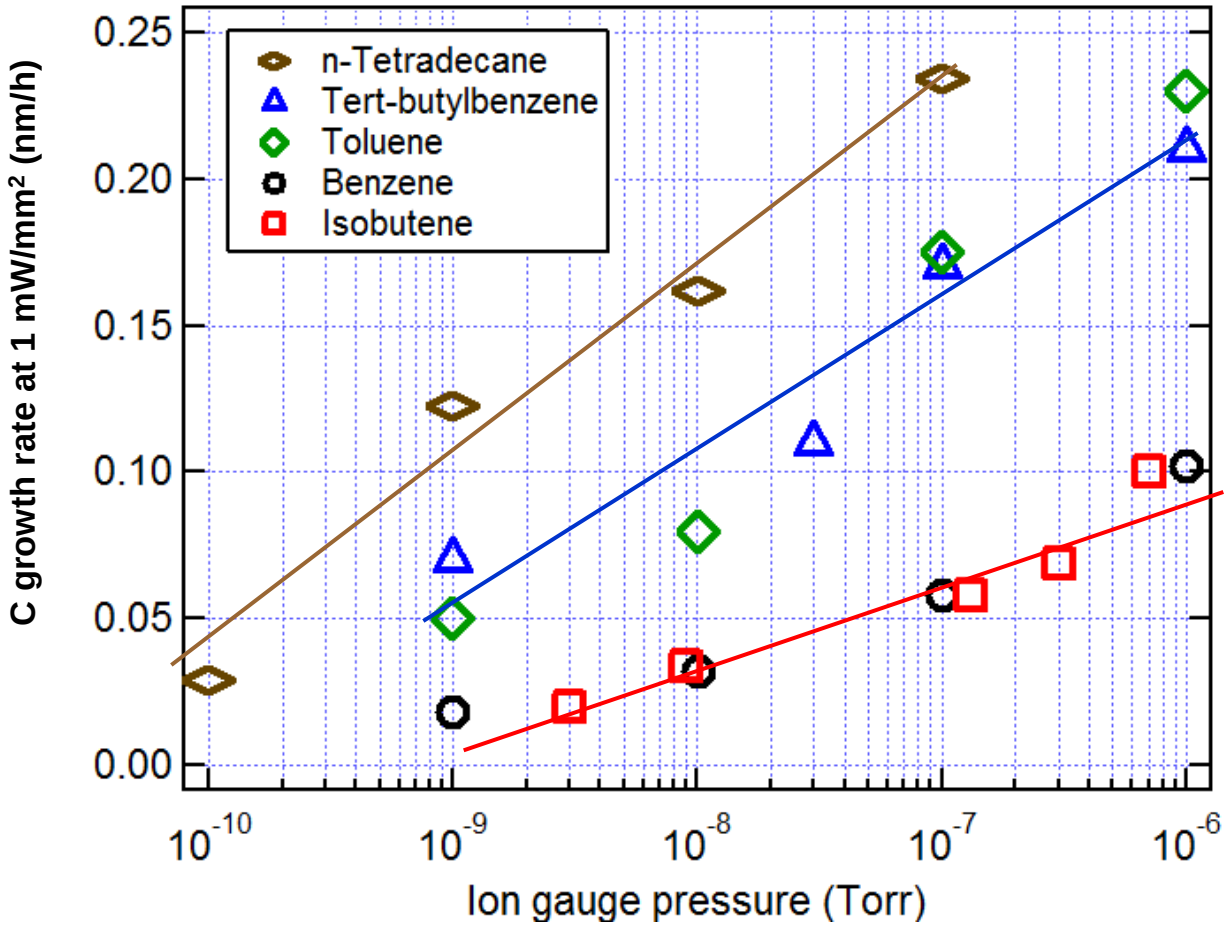



- C growth rate is *mass limited* for $I > I_{sat}$
  - Every adsorbed molecule photo-reacts.
  - Outgas test measures absolute max rate
  - Scales *linearly* with pressure
- $I_{sat}$ increases with pressure.

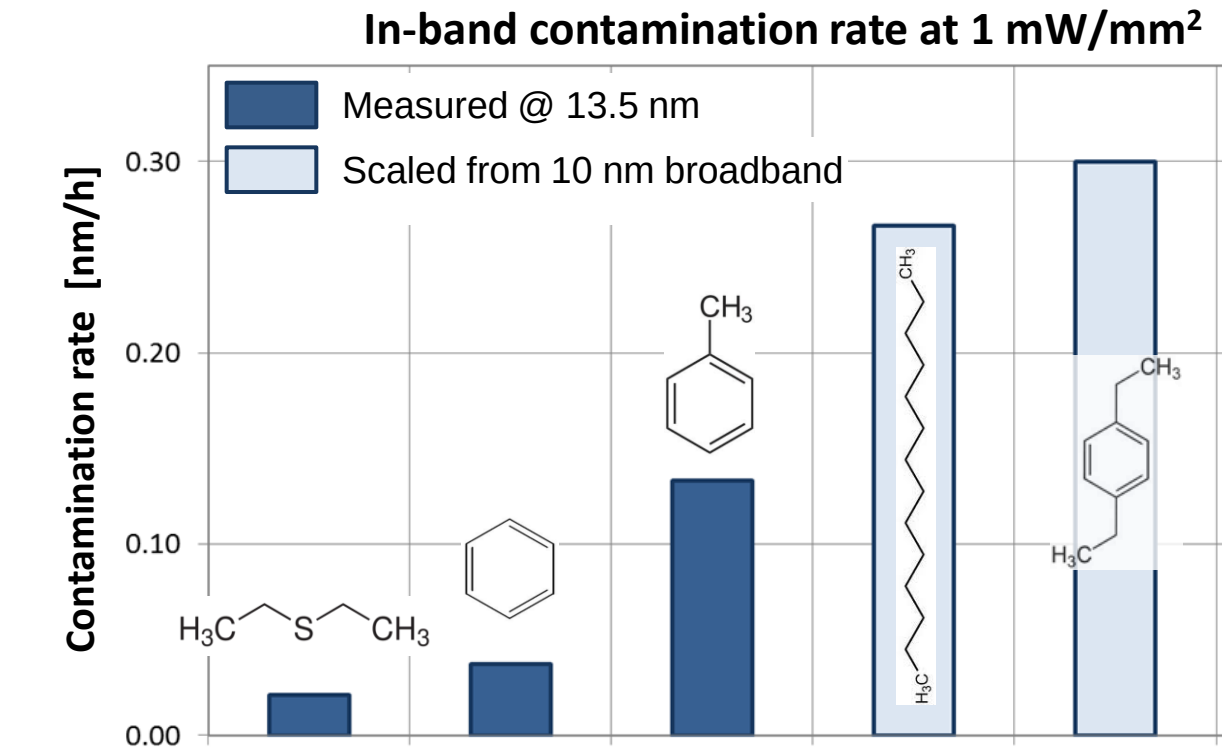
- $I_{sat}$ varies with species.
- Pressure scaling *logarithmic* for $I < I_{sat}$
- Measurement at single P and I cannot be reliably scaled to different conditions.
- Scaling regime must be determined.

# Contamination rates measured over large pressure range



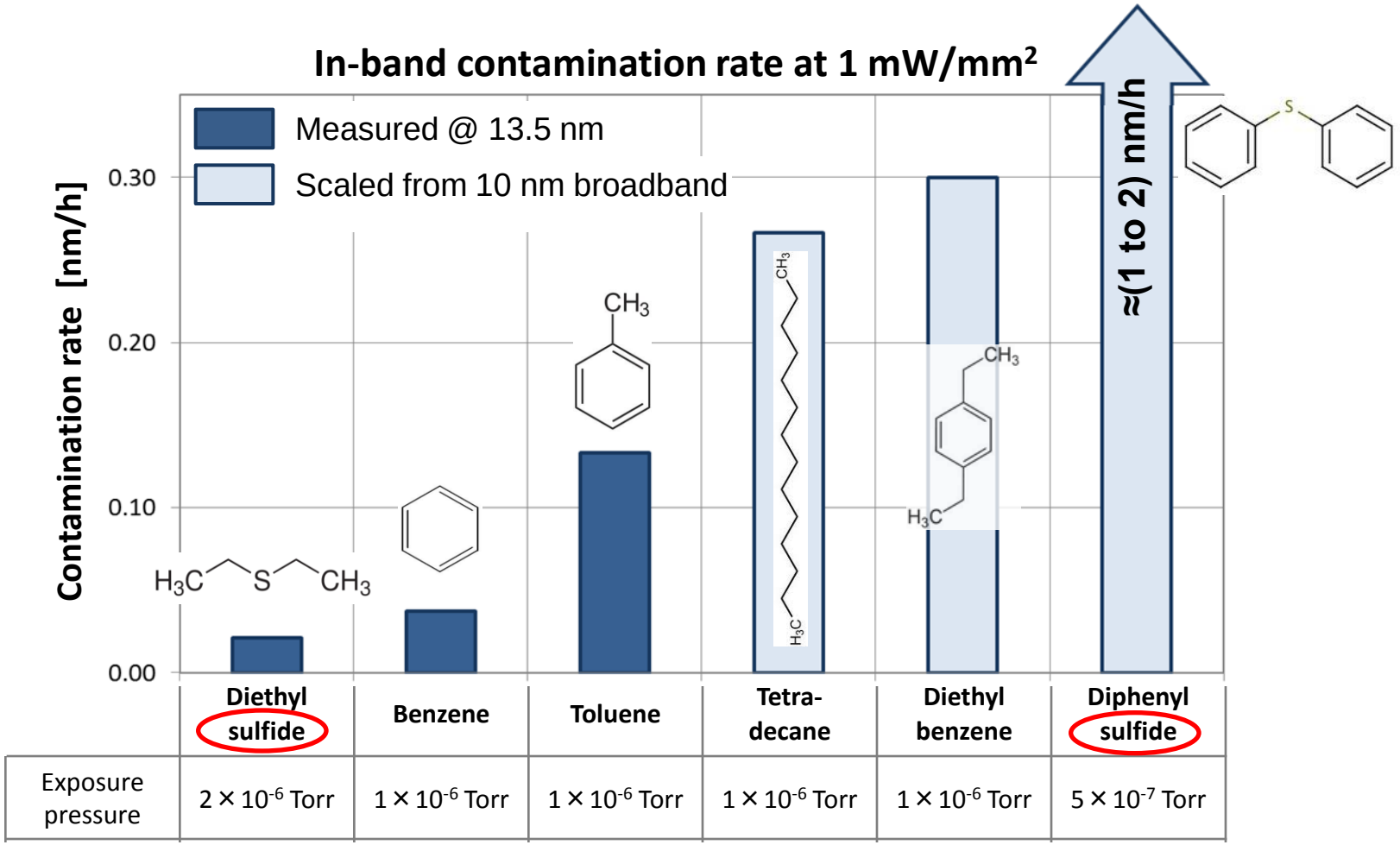

- At 1 mW/mm$^2$ the 13.5 nm contamination rates scale with log of pressure below $10^{-5}$ Torr for every species tested.
- Consistent with non-ideal surface with distribution of adsorption energies.

# Contamination rates below intensity saturation



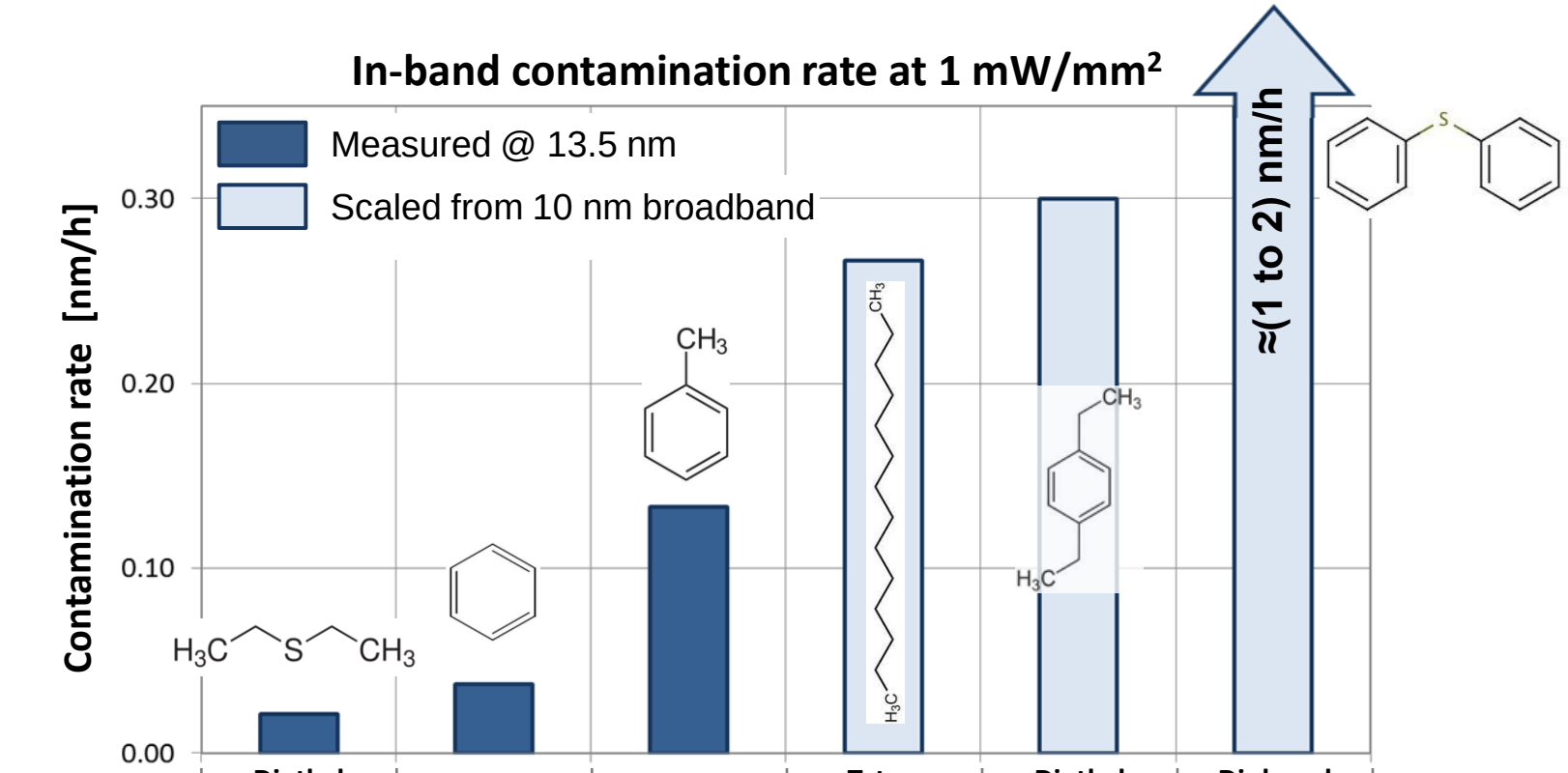

| | Diethyl sulfide | Benzene | Toluene | Tetra-decane | Diethyl benzene |
|---|---|---|---|---|---|
| Exposure pressure | $2 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr |

# Contamination rates below intensity saturation




- Presence of S does not necessarily result in high contamination rate

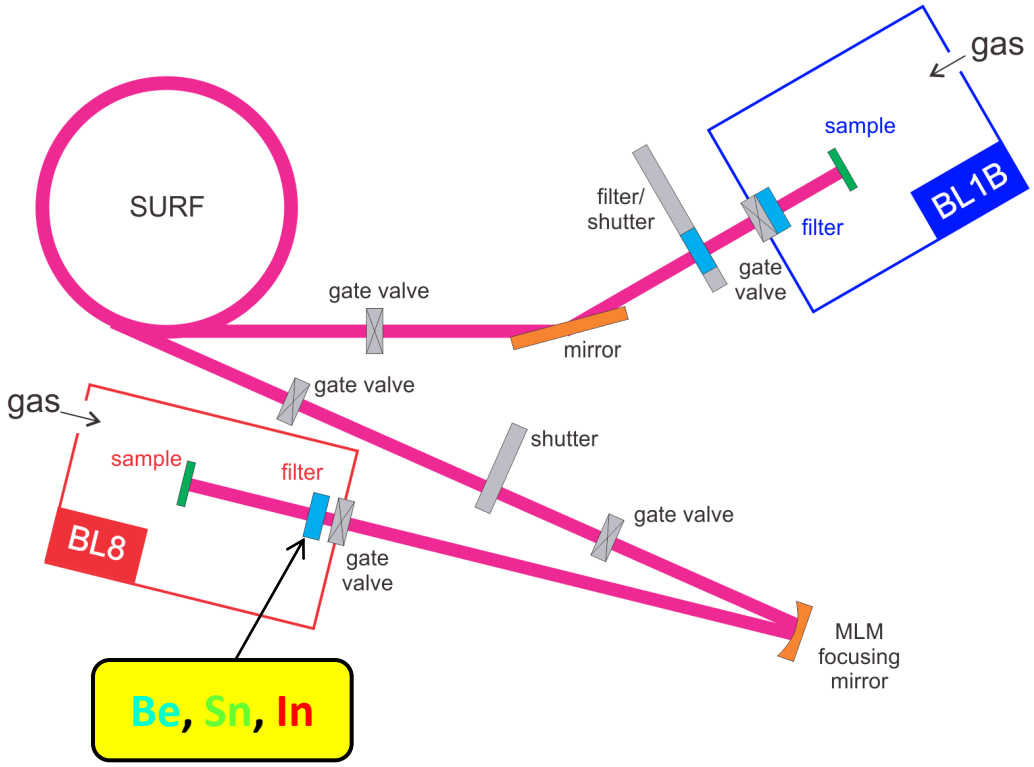
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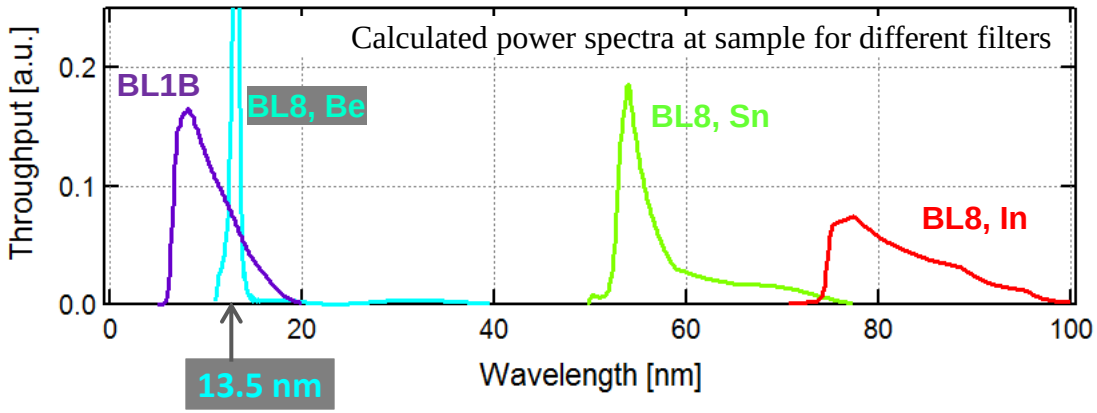

| | Diethyl sulfide | Benzene | Toluene | Tetra-decane | Diethyl benzene | Diphenyl sulfide |
|---|---|---|---|---|---|---|
| Exposure pressure | $2 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $1 \times 10^{-6}$ Torr | $5 \times 10^{-7}$ Torr |
| Vapor pressure | 58 Torr | 94 Torr | 27 Torr | $3 \times 10^{-3}$ Torr | 1 Torr | $2 \times 10^{-3}$ Torr |

- Presence of S does not necessarily result in high contamination rate
- Vapor pressure better indicator of contamination potential, but not universal

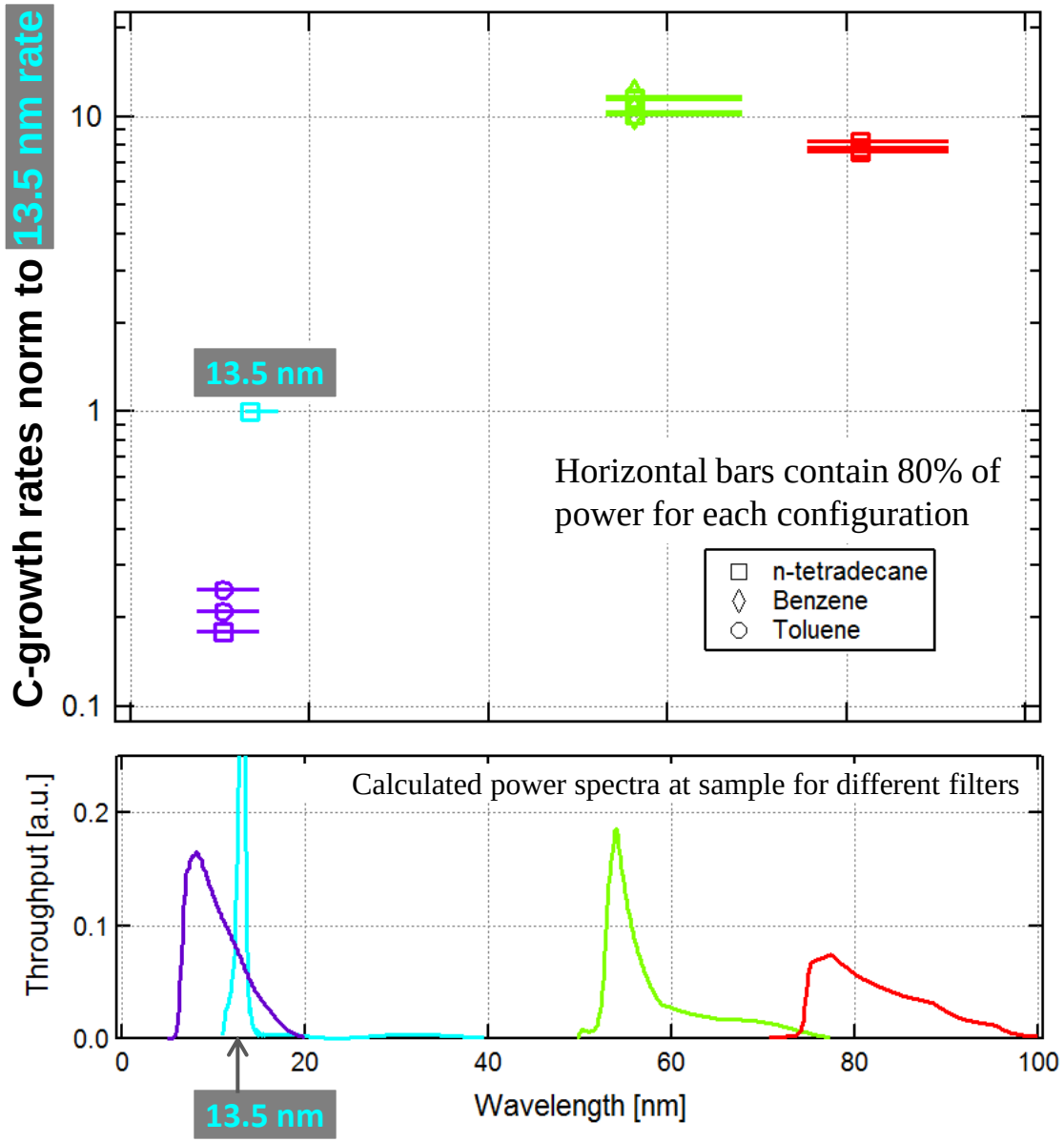
# Wavelength dependence of contamination rates




- Compare ratio of rates at different wavelengths to **"in band" rates at 13.5 nm.**

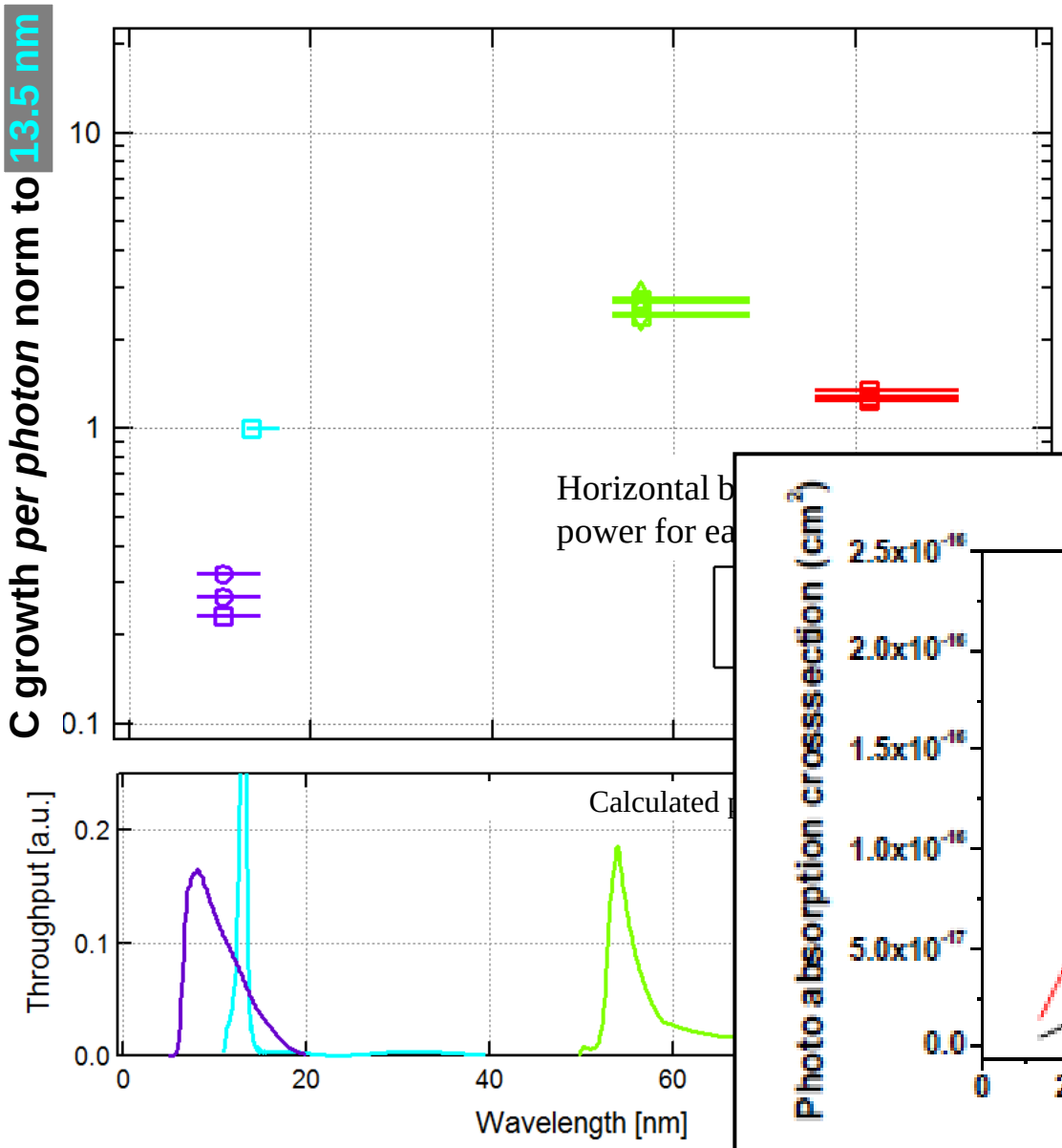


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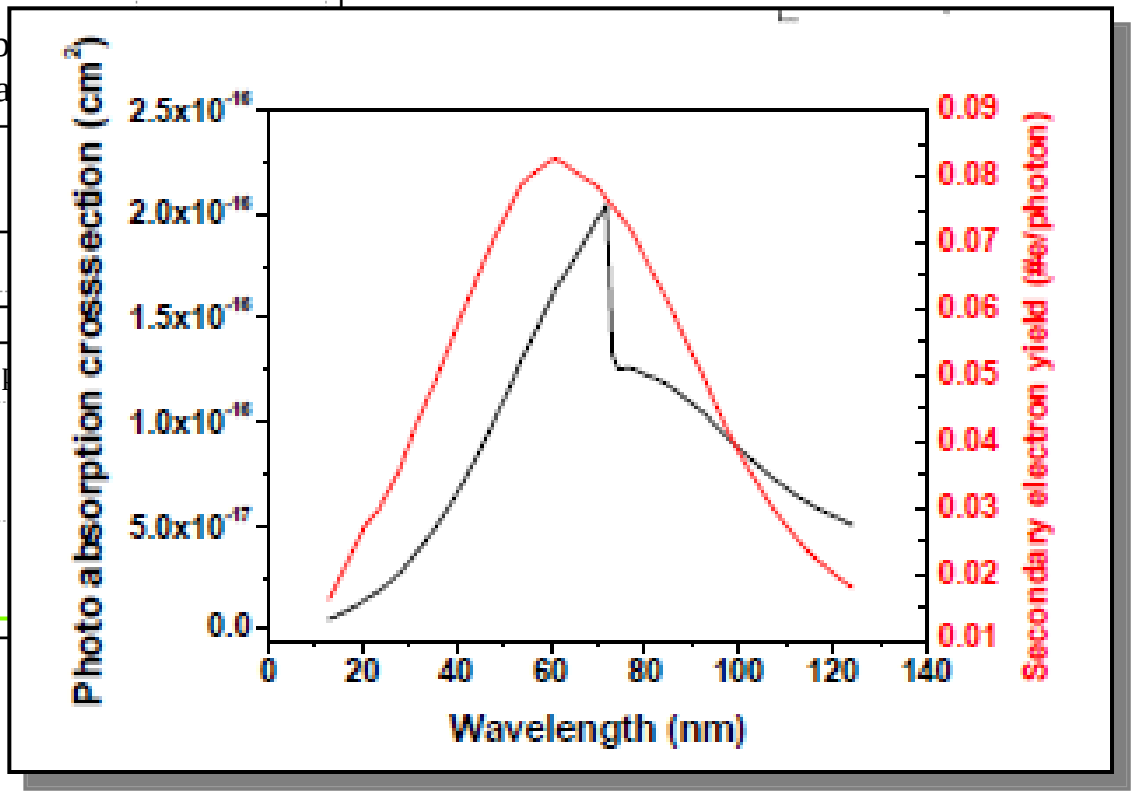



- Compare ratio of rates at different wavelengths to **"in band" rates at 13.5 nm.**
- dramatic increase between ~10 nm and ~60 nm is the same for
  - High & low contaminating species
  - Pressures ($10^{-8}$ to $10^{-6}$) Torr
- Subsequent measurements suggest rates from (100 to 200) nm are comparable to 13.5 nm.
- **DUV out-of-band light may pose greater risk to optics than in-band 13.5 nm light**

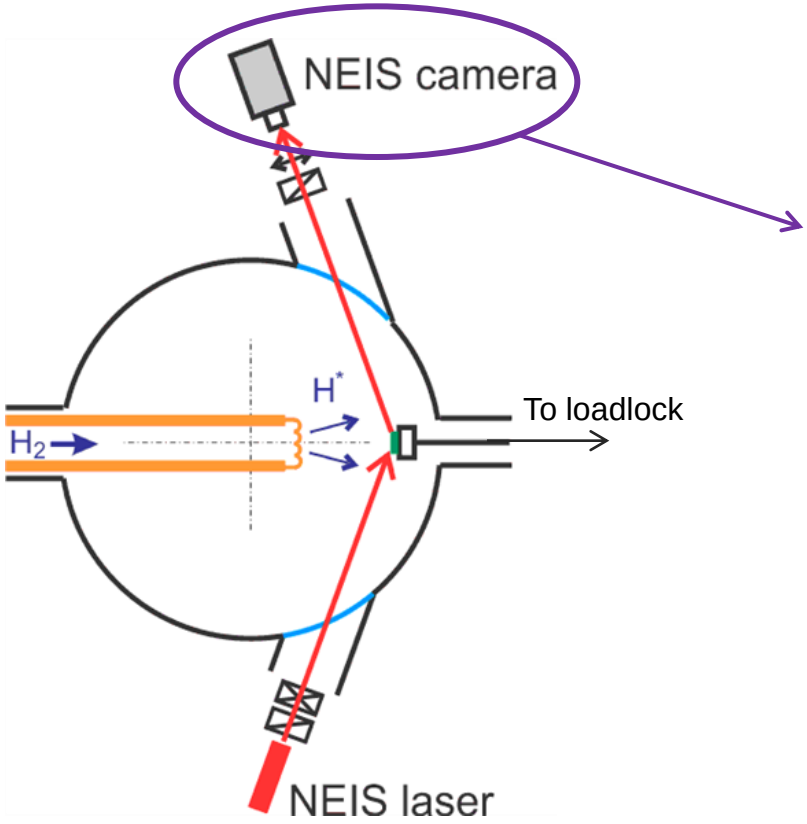
# Wavelength scaling of C deposition *per photon*



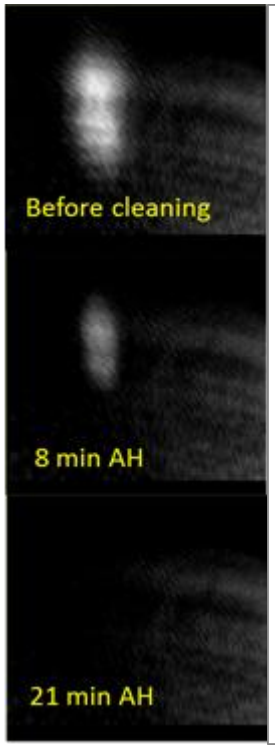

- Contamination per photon also shows significant increase.
- Higher rates not *only* due to increase in photons per unit energy.

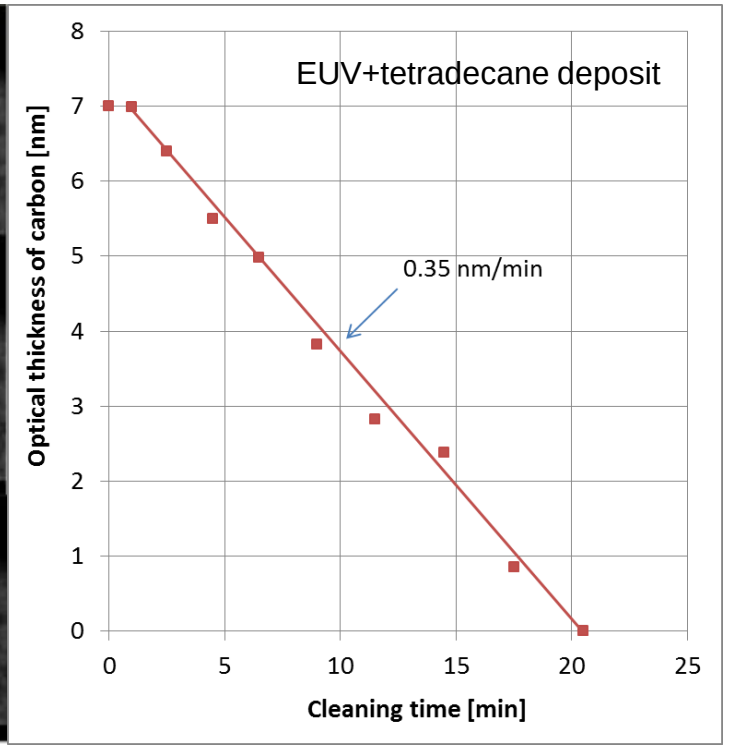


# NIST atomic-H cleaning facility




Cleaning rate determined by in situ
Nulling Ellipsometric Imaging System (NEIS)




- Base pressure ~1E-8 torr
- Filament-sample distance = 45 mm
- Filament material - W
- $H_2$ pressure ~ 1 Torr
- $T_{filament}$ = 1850°C
- $T_{sample} \leq 60°C$

- *In situ* NEIS signal normalized to thickness as measured by XPS before cleaning.

# Atomic-H cleaning of non-C contaminants

- At 2011 EUVLS Resist TWG ASML indicated little/no data on efficacy of atomic H cleaning of non-C contaminants (S, P, I, F, etc.)

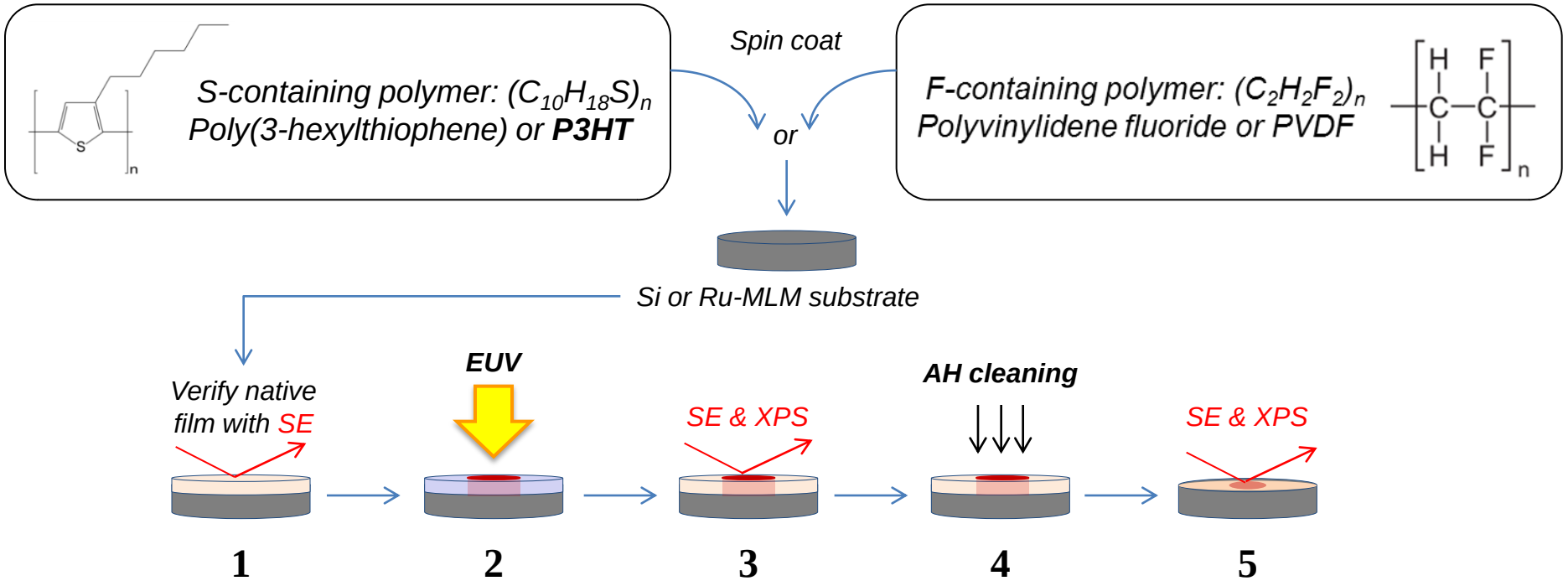
- In **one** case when XPS could be performed before and after cleaning of resist outgas sample, ~3 At% of S was completely removed by AH.

- AH completely removed all C and S from ~6 nm deposit made by exposing $TiO_2$-cap MLM in presence of diphenyl sulfide.

- NIST just completed new "high-contamination" facility to make EUV-induced deposits of highly contaminating species which may contain non-C elements of interest.

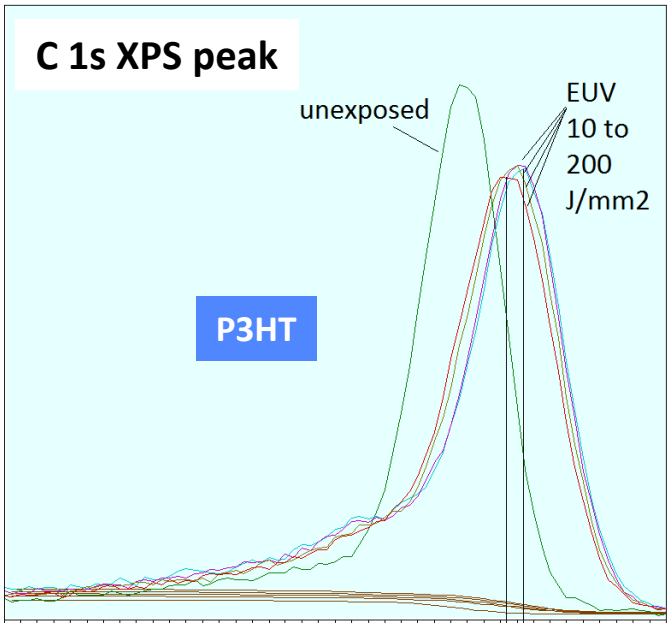
- Prior to this, NIST performed preliminary investigations by AH cleaning of EUV-exposed spin-coated polymers containing appropriate species.

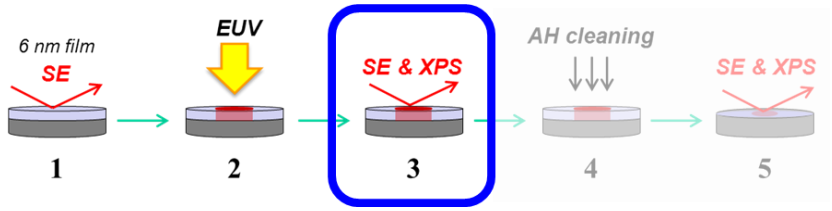
# Polymer-based AH-cleaning study of S & F

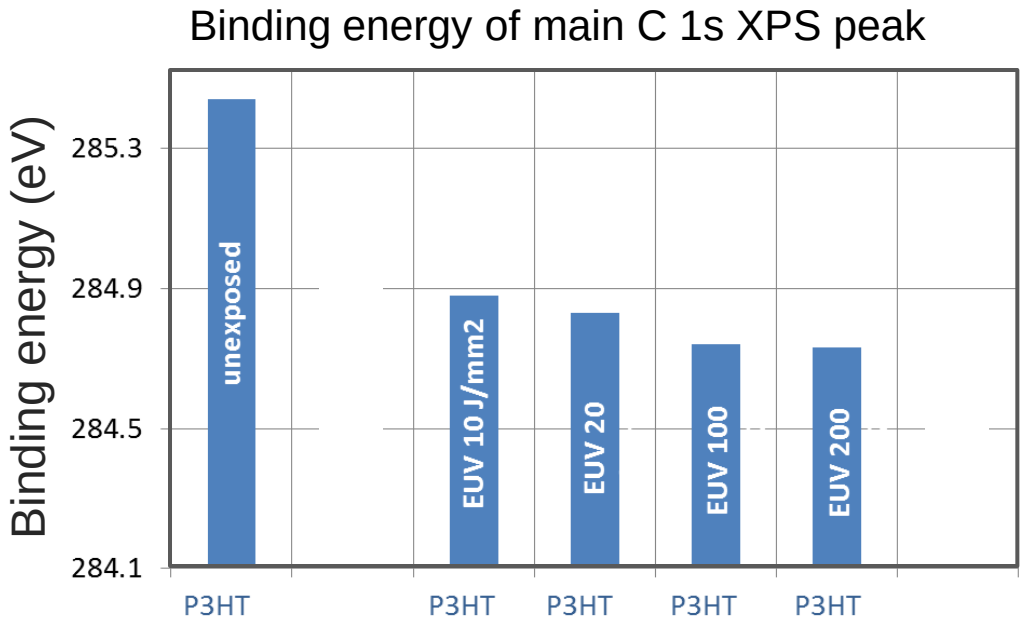



1) Spin coat <10 nm film of polymer onto Si or Ru-cap MLM substrate
2) Perform EUV exposures with varying dose (1-200 J/mm$^2$)
3) Inspect with spectroscopic ellipsometry (SE) and XPS
4) Clean with atomic-H (AH)
5) Inspect with SE and XPS

# Effect of EUV on C 1s XPS peak

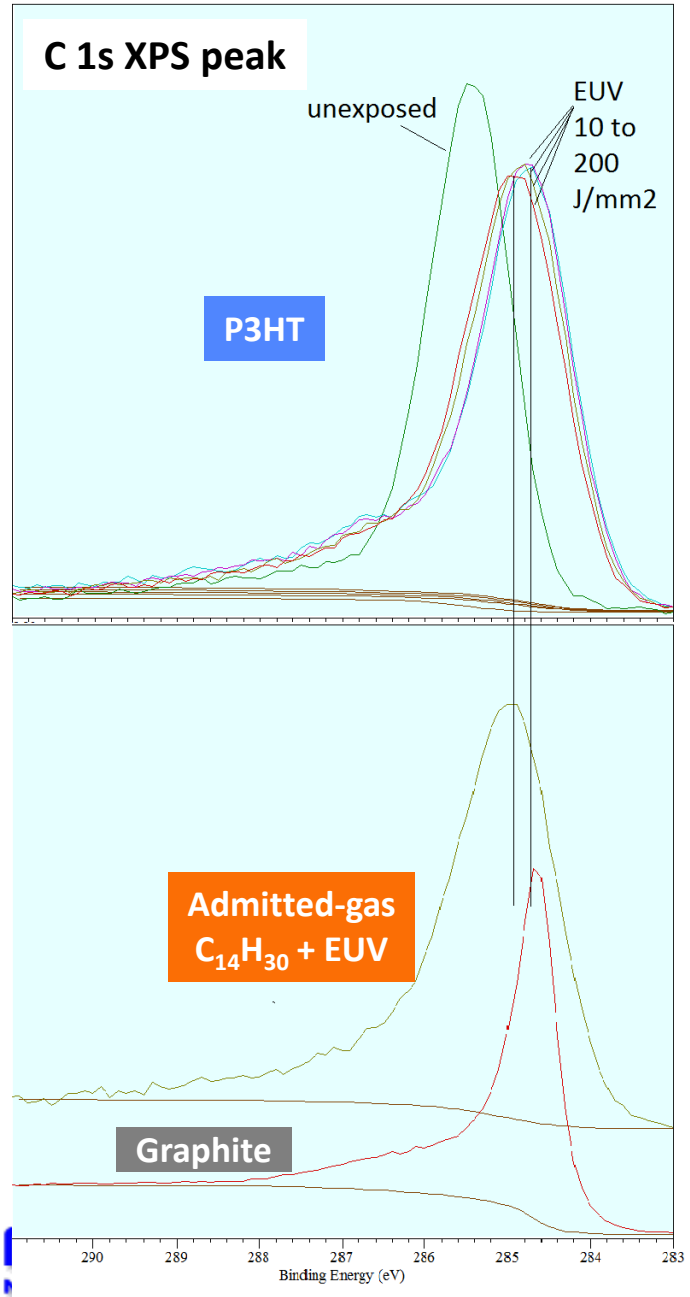


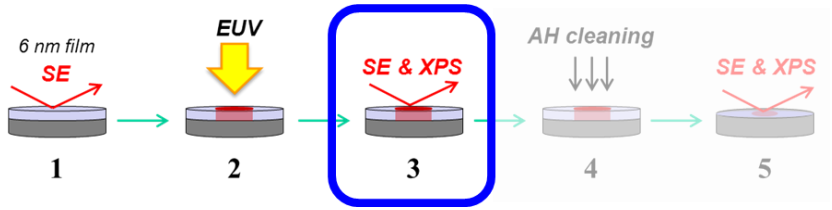



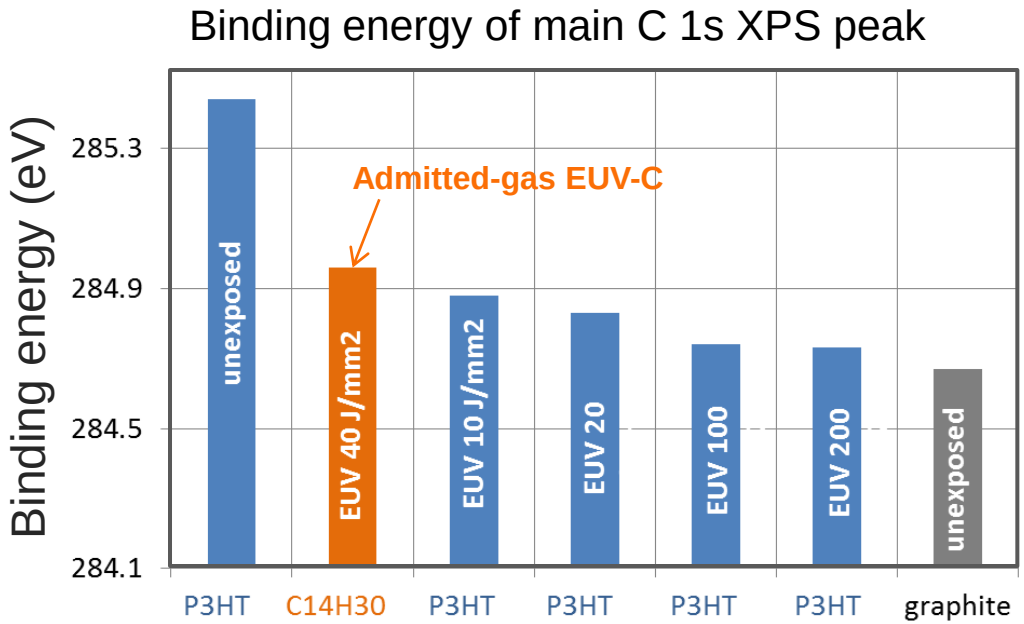




- Lowest EUV dose dramatically alters P3HT C1s peak to similar shape and energy of typical admitted-gas EUV-C.

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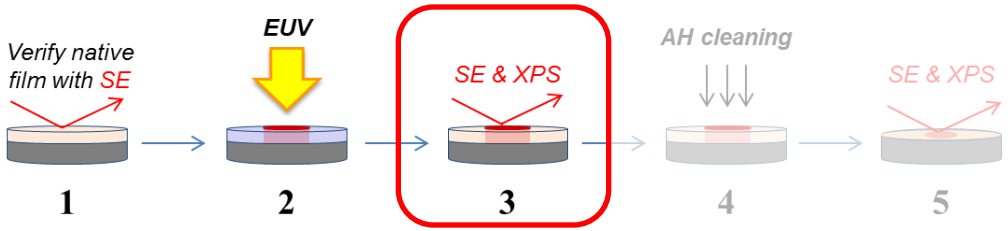


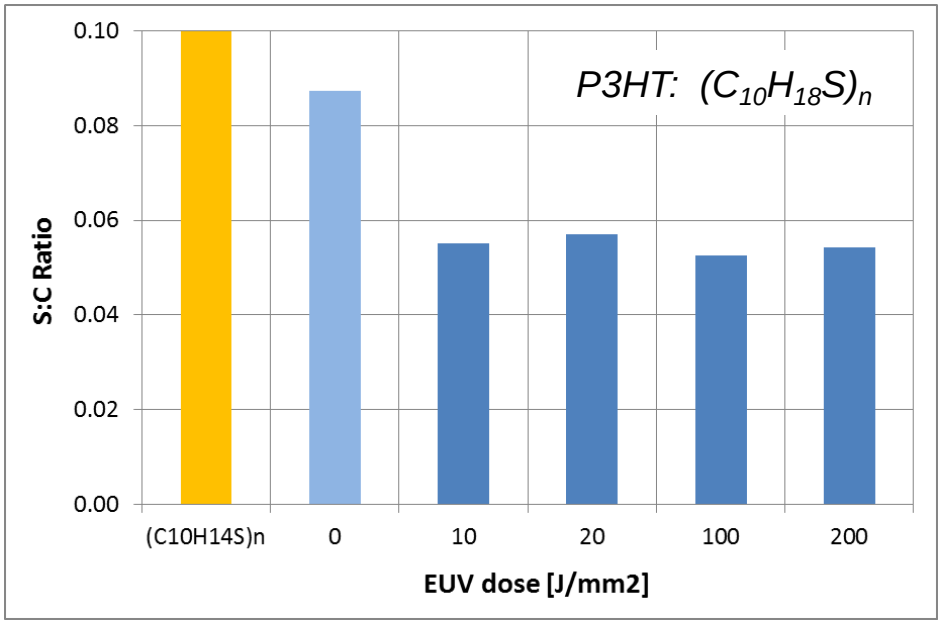




- Lowest EUV dose dramatically alters P3HT C1s peak to similar shape and energy of typical admitted-gas EUV-C.
- C1s binding energy shifts toward graphitic state with increasing EUV dose – as observed with admitted-gas EUV-C deposits.
- Similar trend in PVDF and all admitted-gas exposures

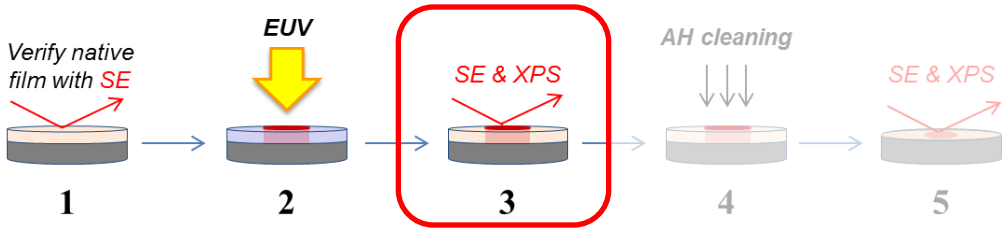
# EUV-induced desorption of S and F

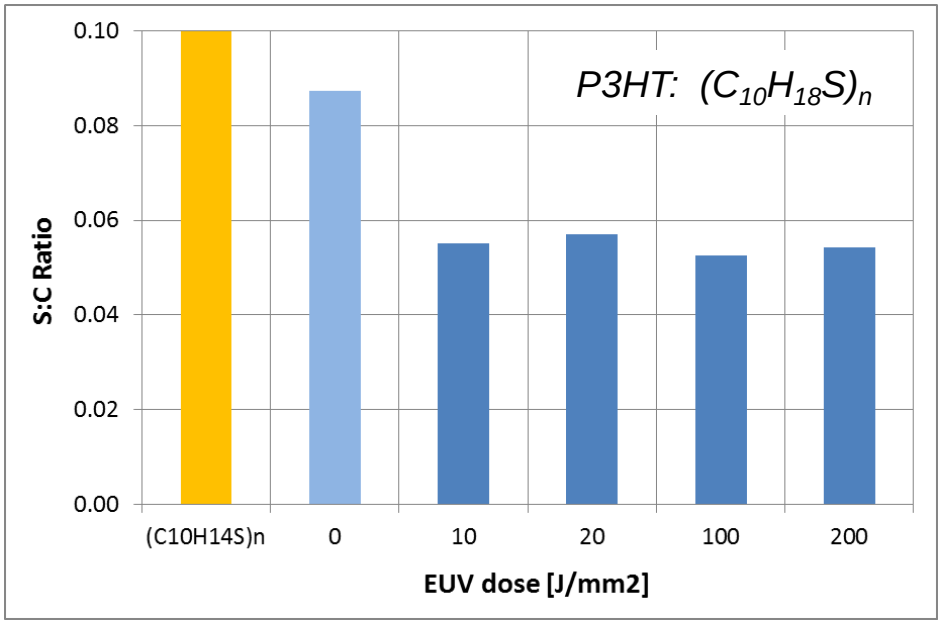


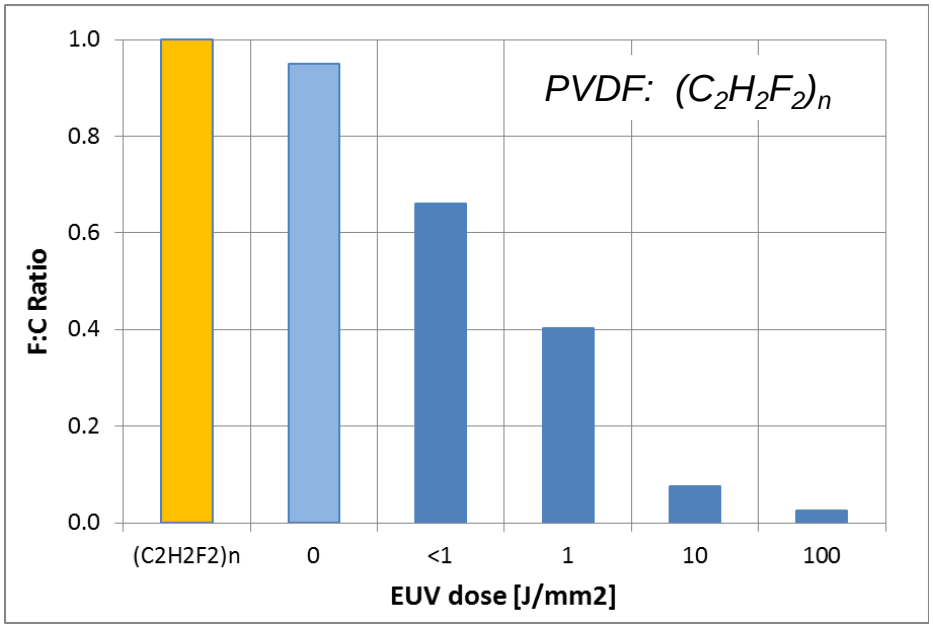




- Amount of C remains relatively constant with EUV dose for both polymers
- S is partially desorbed by EUV
  - ~ 40% of S is rapidly desorbed by EUV (<10 J/mm2)
  - ~60% of S is resistant to desorbtion by highest doses

# EUV-induced desorption of S and F



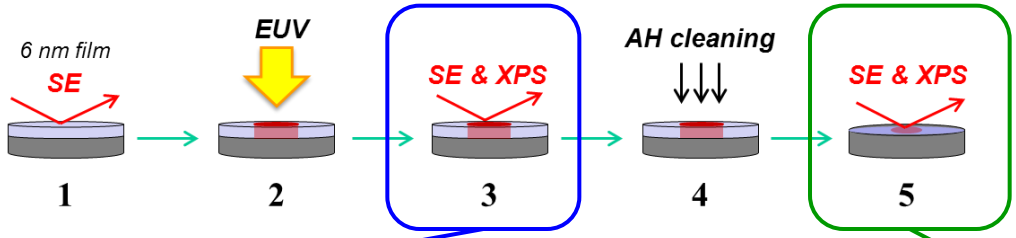




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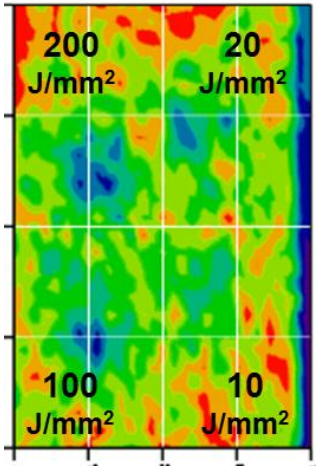
- F is highly susceptible to desorption by EUV
  - ~50% of F is rapidly desorbed by lowest doses
  - F continues to desorb with increasing dose

# AH effectively cleans S-containing polymer




## Before cleaning

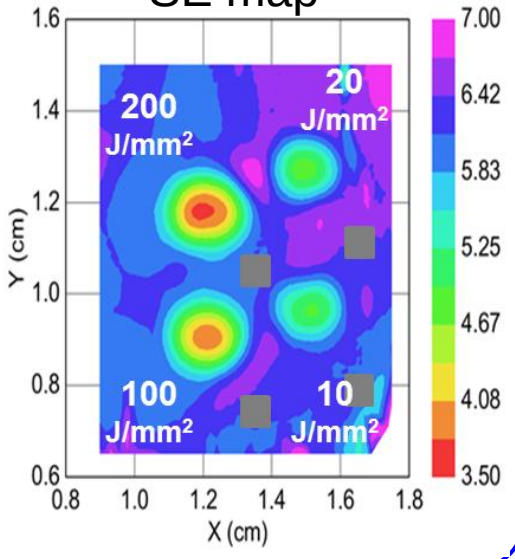
XPS S 2s map




XPS Atomic concentration

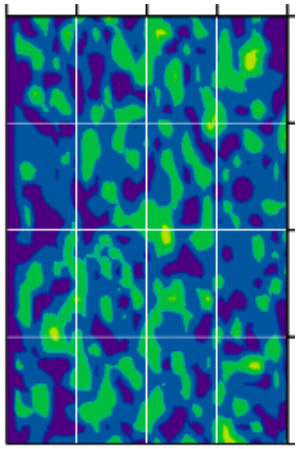
| EUV dose J/mm2 | C 1s at% | O 1s at% | S 2s at% | Si 2p at% | N 1s at% |
|---|---|---|---|---|---|
| 0 | 72 | 11 | 6.3 | 11 | 0.2 |
| 10 | 69 | 16 | 3.8 | 12 | 0.3 |
| 20 | 69 | 16 | 3.9 | 11 | 0.3 |
| 100 | 67 | 16 | 3.5 | 13 | 0.2 |
| 200 | 67 | 17 | 3.6 | 13 | 0.4 |

SE map




## After cleaning

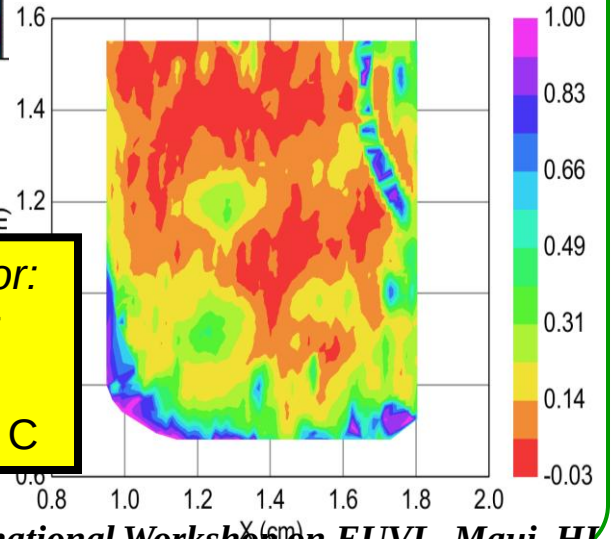
XPS S 2s map



XPS Atomic concentration

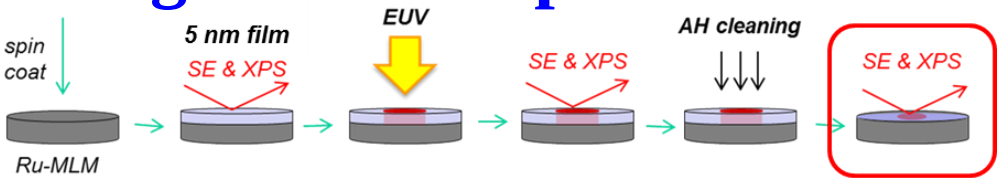
| EUV dose J/mm2 | C 1s at% | O 1s at% | S 2s at% | Si 2p at% | N 1s at% |
|---|---|---|---|---|---|
| 0 | 13 | 34 | <0.5 | 53 | 0.1 |
| 10 | 14 | 34 | <0.5 | 52 | |
| 20 | 14 | 34 | <0.5 | 52 | |
| 100 | 17 | 33 | <0.5 | 49 | |
| 200 | 15 | 35 | <0.5 | 51 | |

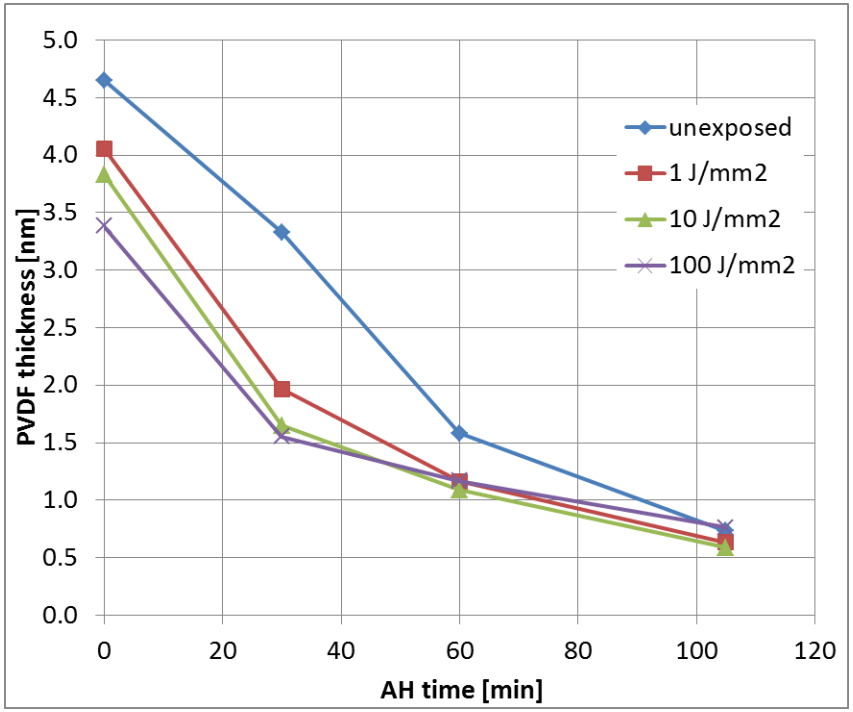
SE map




*Cleaning rate for:*
EUV-polymer
≥
EUV-deposited C

# AH cleaning of EUV-exposed 5 nm PVDF film




- Initial cleaning rate of EUV-exposed (less F) polymer is faster than for native (more F)
- Even fast initial cleaning rate is ~3x slower than rate for EUV-deposited C
- Cleaning rates decrease significantly with time for all EUV doses
- Suggests presence of F hinders AH cleaning.
- Consistent with EIDEC outgas results showing no F in exposure spot but significant F outside, even after AH.

# Important issues in optics contamination

1. **Establish equivalence of e-beam vs. EUV resist outgas testing**
   - Compare C thickness for expanded set of resists
   - Compare AH cleaning efficacy (both C and non-C)

2. **Contamination rates of PAG-related molecules containing (S, F, P, I…)**

3. **AH cleanability of deposits containing S, F, P, I…**
   - Cleaning of contamination from EUV exposure in admitted gases
   - Resist-outgas samples with XPS measurements before and after AH cleaning

4. **Possible new phenomena associated with long-term EUV exposure in HVM:**
   - "graphitization" of C and impact on AH cleaning rate
   - Reflectivity loss due to repeated AH cleaning

5. **Further improvements in the XPS determination of residuals**
   - Developing methods for common definition of "detection limit"
   - Compare non-C At% for outgas-test residuals with different labs


intel


ASML


SEMATECH


RUTGERS
THE STATE UNIVERSITY
OF NEW JERSEY

***Thank you!***


THE JOHNS HOPKINS UNIVERSITY BALTIMORE
1876
VERITAS VOS LIBERABIT


UNIVERSITY of VIRGINIA

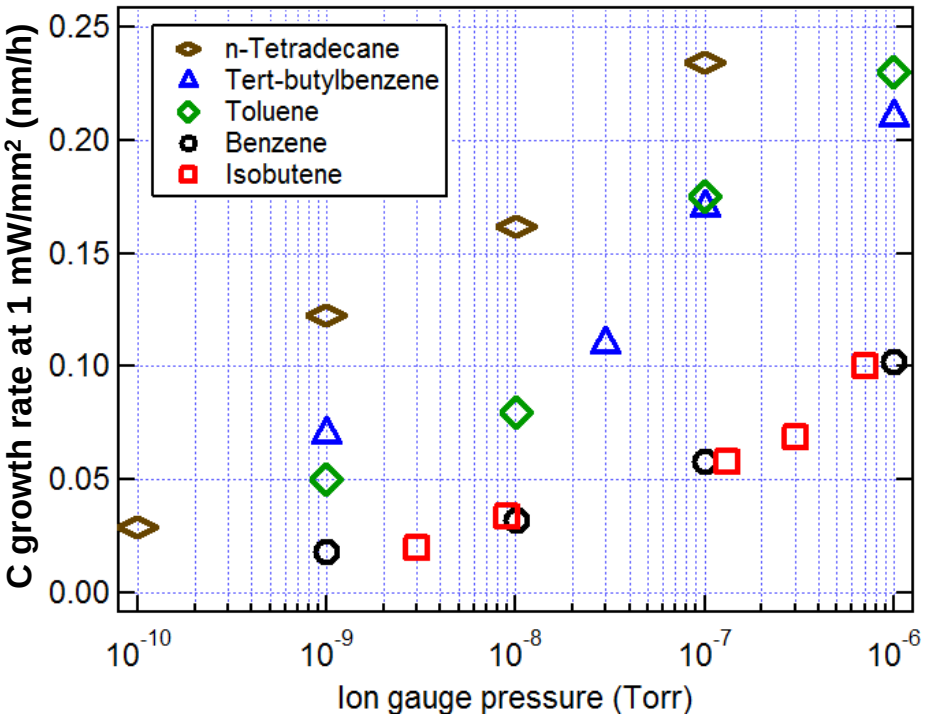

BERKELEY LAB


IOF

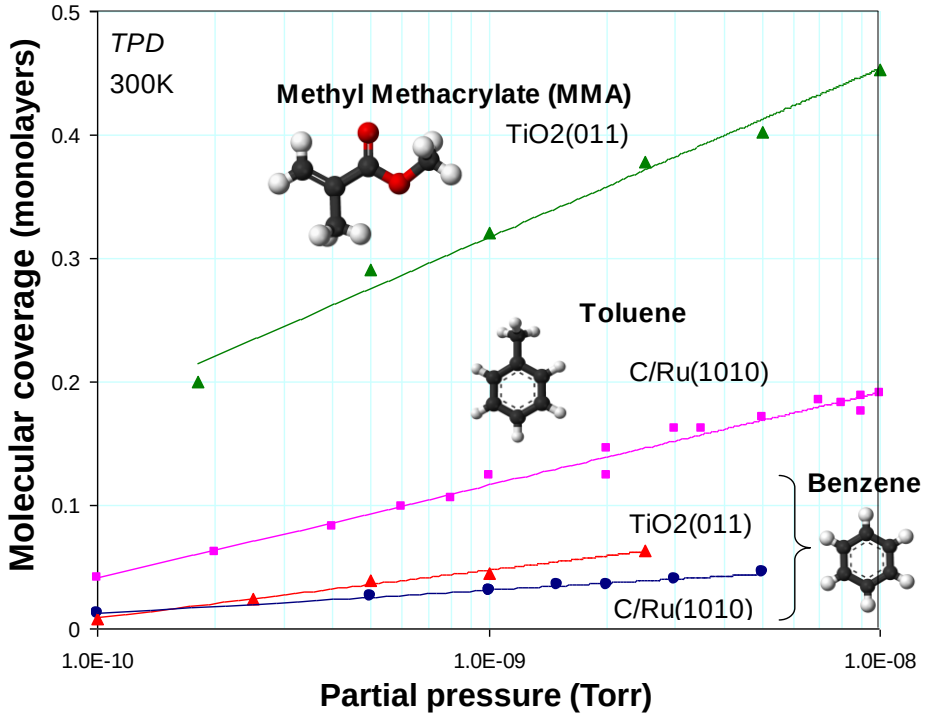
# Supplemental Slides

# Pressure scaling of EUV contamination rates driven by fundamental surface physics

**EUV-induced contamination rates (NIST)**

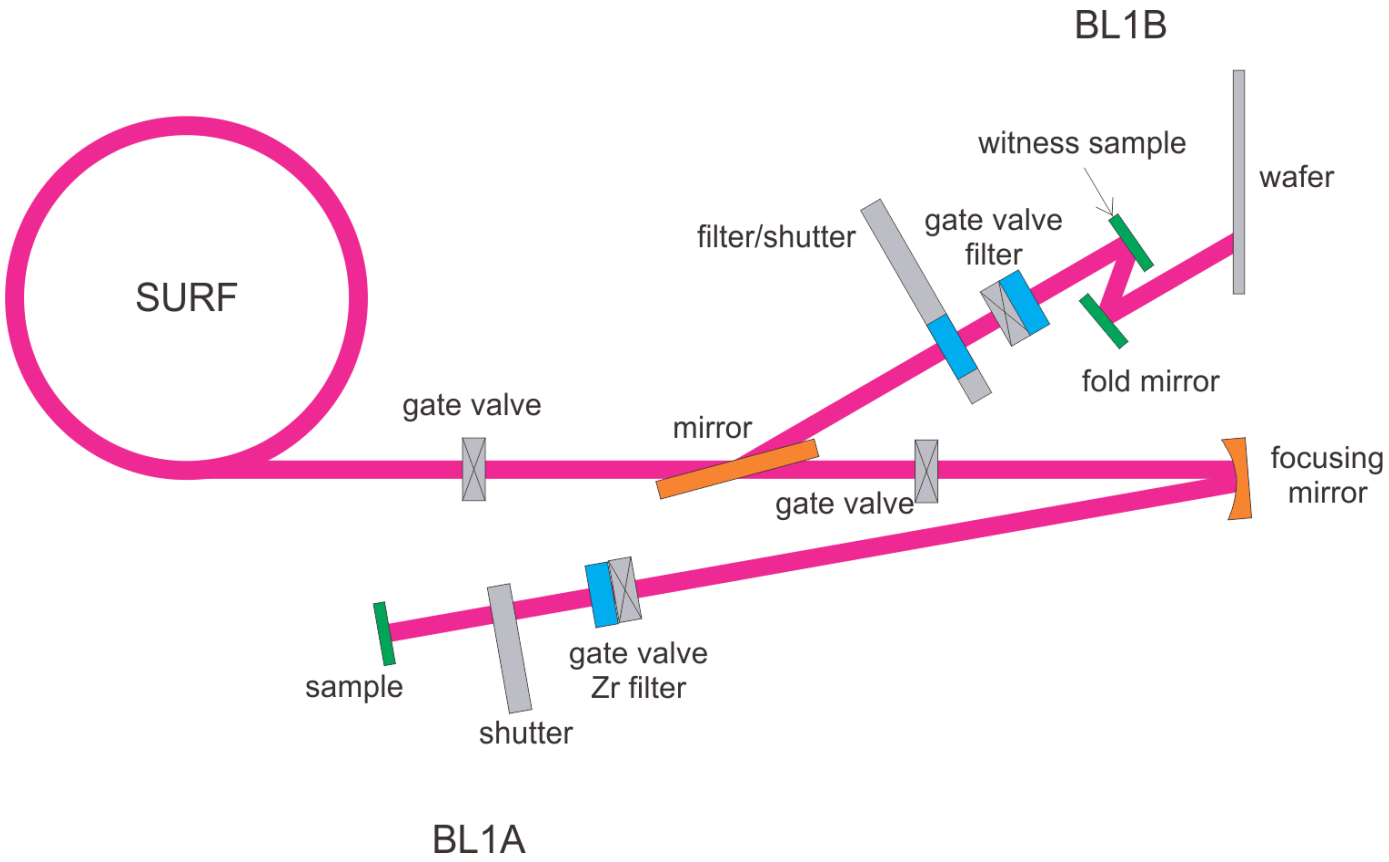



**Equilibrium coverage (Rutgers, *no EUV*)**



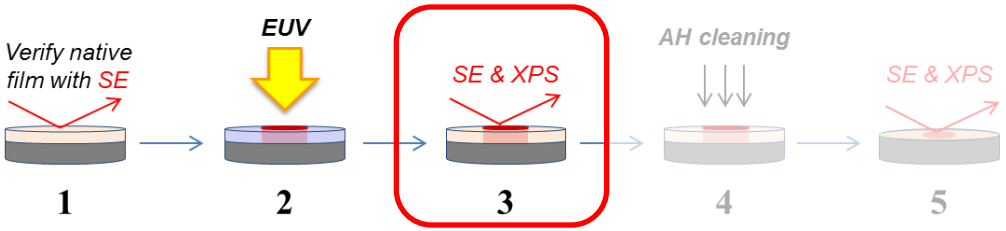

- EUV contamination *and* equilibrium molecular coverage (non-irradiated) scale with log of pressure
- Additional measurements at Rutgers show surface binding energy decreases with coverage, leading to sub-linear pressure dependence of coverage.

# New facility for highly contaminating molecules

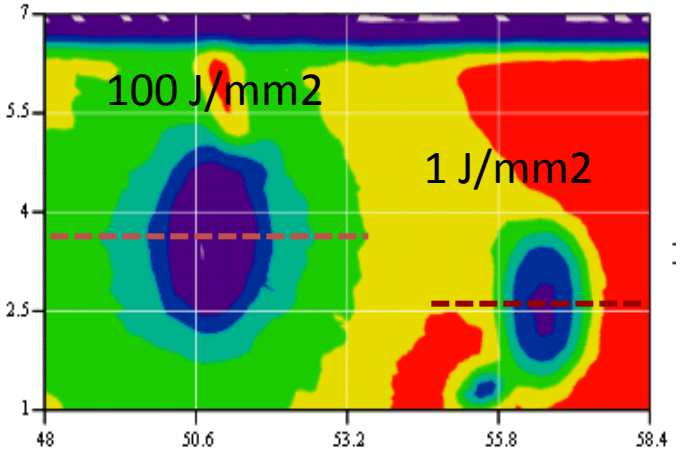



- PAG related molecules containing S, P, I, F, etc.

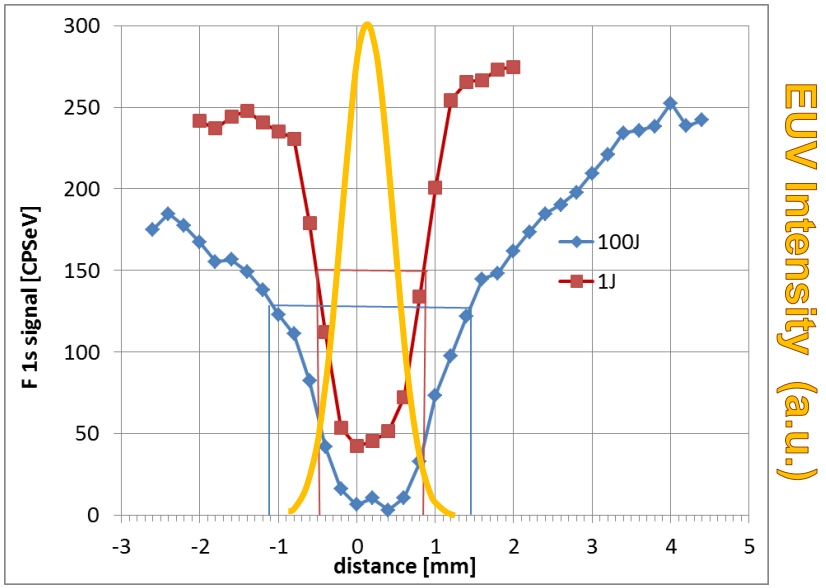
# EUV-induced F desorption from 15 nm PVDF film




XPS F1s map (2 exposures)




Line profiles of XPS F1s map




- XPS of 5 & 15 nm films shows F is rapidly desorbed from polymer by EUV, but C is not.
  - DEA cross section of adsorbed halocarbons is VERY high [e.g. ~4x10^-16 cm2 for CF2Cl2/Ru in JCP 121(17) (2004) 8547]
- Similar EUV exposures of S-containing polymer produced only ~25% reduction in S:C ratio.